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Developing Standards for Dissolved Iron in Seawater

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In nearly a dozen open-ocean fertilization experiments conducted by more than 100 researchers from nearly 20 countries, adding iron at the sea surface has led to distinct increases in photosynthesis rates and biomass. These experiments confirmed the hypothesis proposed by the late John Martin [Martin, 1990] that dissolved iron concentration is a key variable that controls phytoplankton processes in ocean surface waters. However, the measurement of dissolved iron concentration in seawater remains a difficult task [Bruland and Rue, 2001] with significant interlaboratory differences apparent at times. The availability of a seawater reference solution with well-known dissolved iron (Fe) concentrations similar to open-ocean values, which could be used for the calibration of equipment or other tasks, would greatly alleviate these problems [National Research Council (NRC), 2002].

The Sampling and Analysis of Fe (SAFe) cruise was staged from Honolulu, Hawaii, to San Diego, Calif., between 15 October and 8 November 2004 to collect data and samples that were later used to provide this reference material. Here we provide a brief report on the cruise results, which have produced a tenfold improvement in the variability of iron measurements, and announce the availability of the SAFe dissolved Fe in seawater standards.

The Need for the SAFe Cruise

A 2002 Workshop on Iron Dynamics in the Carbon Cycle [Johnson *et al.*, 2002] pointed to the need for basin-scale surveys of iron distributions. Since then, new, international programs such as GEOTRACES (<http://www.geotraces.org>) have been created with a goal of determining “full water column distributions of selected trace elements... along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions.” However, this goal cannot be reached if there is inconsistency in the results obtained by each laboratory that participates.

A blind comparison of iron measurements was made during 2001 and 2002 by 24 labora-

tories from nine nations on subsamples of a single surface water sample from the Atlantic Ocean [Bowie *et al.*, 2006]. The range of the average values reported by each laboratory (0.2 to 1.2 nanomoles per liter, ignoring three outliers of much greater concentration) was larger than the concentration difference from the surface to deep (<1000 meters) waters in most of the Pacific Ocean. Also, the concentration of iron in these solutions analyzed over time by one laboratory showed an initial, rapid increase followed by a slower decrease, indicating imperfect preservation of the iron in solution.

With this as background, the SAFe cruise, funded by the U.S. National Science Foundation, had two primary goals. The first goal involved collecting large volumes of uncontaminated seawater to be used as reference materials for dissolved Fe analysis. The second involved conducting onboard ship experiments to produce an extensive intercomparison of sampling, processing (including filtration), and analytical techniques for dissolved iron and iron speciation measurements.

Making accurate measurements of iron at very low concentrations presents a challenge. However, areas of the ocean that have low concentrations of iron are among the most interesting because the low iron concentrations limit phytoplankton growth. Scientists decided that the major activity of the

cruise should take place around 30°N, 140°W to ensure that seawater with low iron concentrations was obtained for the reference material and for the analytical intercomparisons. This site was sampled twice in the 1980s and once in 2002. During these previous tests, surface water iron concentrations were low at less than 0.1 nanomole per liter.

The SAFe Cruise

Thirty-two scientists representing 18 laboratories (Table 1) from eight countries participated in the cruise. These scientists were prepared to make iron measurements by the major techniques now used in the field and in shore-based laboratories. These methods included three types of cathodic stripping voltammetry, three types of flow injection analysis (FIA), and, in shore-based laboratories, measurements by graphite furnace atomic absorption spectrometry and inductively coupled plasma-mass spectrometry (ICP-MS).

Initial comparisons of iron measurements made at sea on samples from 1000 meters showed large differences, with many of the results substantially lower than expected. The apparent low bias suggested that iron was not being fully recovered. A series of experiments conducted at sea led to the conclusion that sample preparation was a key step in analyzing freshly collected seawater. Acidification of samples to a pH of at least 1.8 was required to release all of the iron from bonds with organics, thus making it available for analysis. Other approaches to sample preparation, such as microwaving, were partially tested and appear promising.

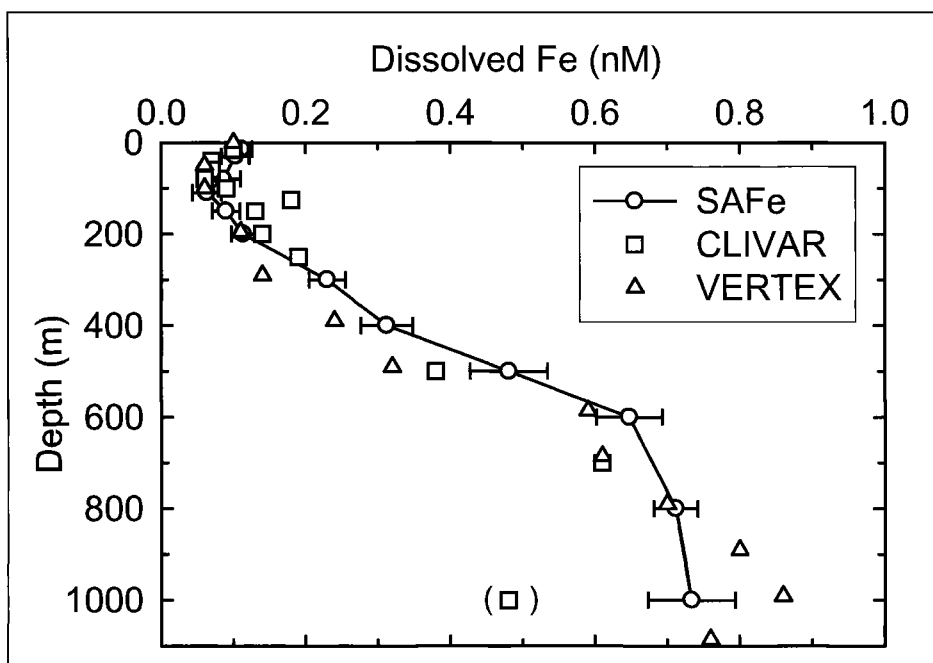


Fig. 1. Dissolved iron profile at the Sampling and Analysis of Fe (SAFe) station (30°N, 140°W) measured on board ship during the SAFe cruise (circles), during the Vertical Transport and Exchange (VERTEX) program in 1986 by OE/GFAAS (triangles) [Martin *et al.*, 1988], and during the Climate Variability and Predictability (CLIVAR) P2 cruise in 2004 by FIA/DPD (squares) (C. Measures, unpublished data, 2006).

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It was also determined that much of the dissolved Fe(III) was reduced to Fe(II) when the sample was acidified only with hydrochloric acid (HCl). This causes a low bias in methods that might select against Fe(II). Adding hydrogen peroxide (H_2O_2) to a final concentration of 10 micromoles per liter was sufficient to reoxidize all Fe(II) to Fe(III) before analysis.

There was a substantial improvement in analytical agreement for different methods used on the same sample of water when samples were prepared in a uniform manner. The concentrations of iron in a vertical profile that were averaged from nine different analytical techniques on board the ship are shown in Figure 1. This profile is compared with vertical profiles of iron determined at nearby stations in 1986 during the Vertical Transport and Exchange (VERTEX) program and in 2004 on the Climate Variability and Predictability (CLIVAR) P2 Repeat Hydrography cruise.

The agreement in data between the SAFE profile and the CLIVAR and VERTEX profiles reveals that representative samples were collected. The agreement also ties the work of a broad segment of the community to the historical database and to an ongoing global iron measurement program.

Dissolved Iron in Seawater Reference Materials

The concentration of a chemical reference material is normally assigned by an analytical method such as isotope dilution ICP-MS that readily establishes traceability in measured results through an unbroken chain of comparisons to recognized standard quantities [NRC, 2002]. However, the concentration of iron in seawater is so low that chemical blanks and contamination make direct assessment of traceability difficult, if not impossible. The seawater samples collected on the SAFE cruise were therefore assigned consensus concentrations, which represent the average value determined through interlaboratory testing [NRC, 2002].

Three sets of samples, which could be used as consensus reference materials for dissolved iron, were collected at the station mentioned in Figure 1. A 1000-liter surface sample was obtained using a trace-metal clean pumping system (S1), and two separate 500-liter lots of seawater from 1000 meters were collected with Go-Flo sampling bottles (D1 and D2). Each of the large-volume, open-ocean samples was filtered into a 1000-liter tank using 0.2-micrometer Poretics cartridge filters, homogenized, and then subsampled into ~600 precleaned, 500-milliliter low-density polyethylene bottles on board ship. Samples were acidified to pH 1.8 using high-purity, sub-boiling quartz distilled HCl prepared at the University of California, Santa Cruz laboratory.

The open-ocean samples have been analyzed at sea and ashore by most of the laboratories that participated in the SAFE cruise.

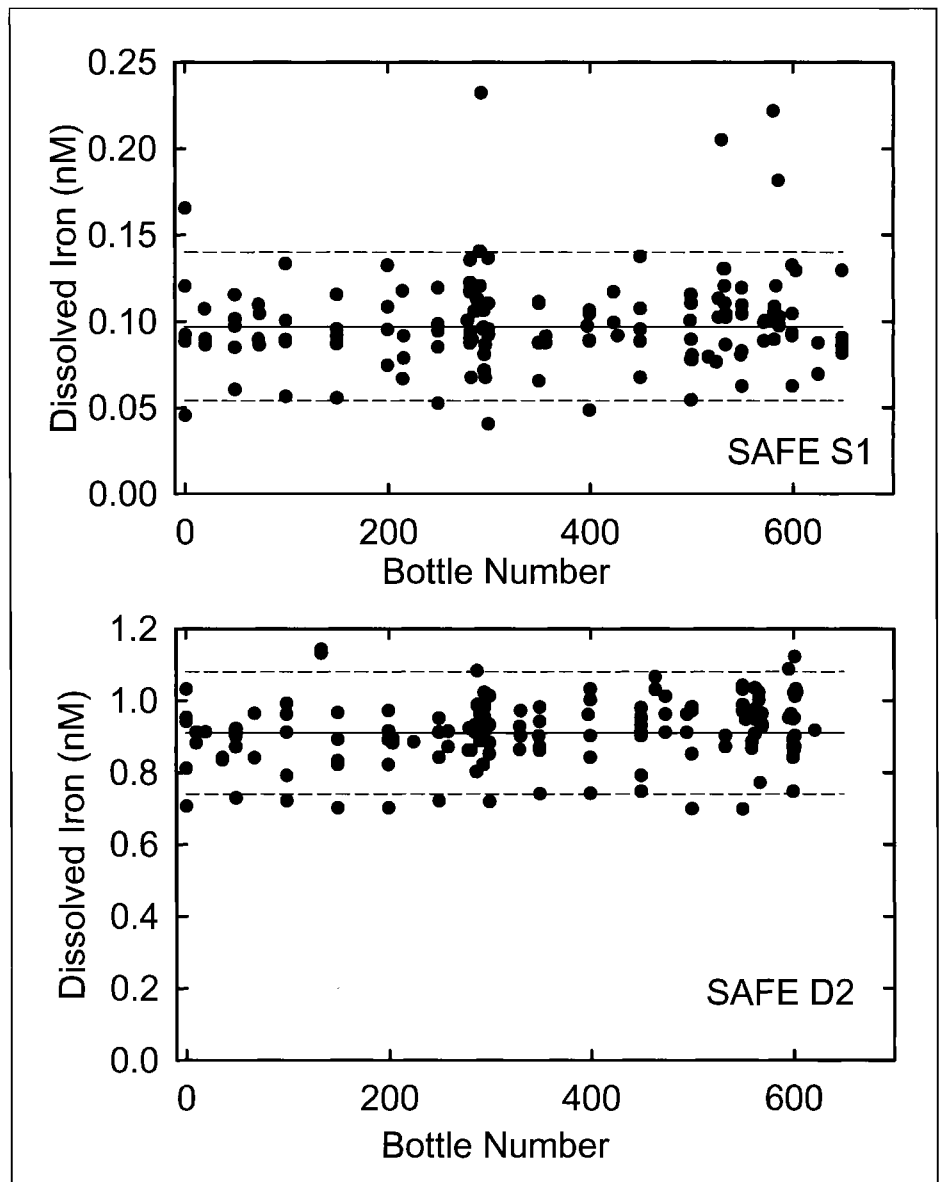


Fig. 2. Dissolved iron concentration versus bottle number in the (top) S1 and (bottom) D2 reference materials. Results represent 140 values reported for 47 bottles of S1 and 168 values for 46 bottles of D2. Mean values are reported if replicate measurements were made on one day. The figure includes results from 19 analysts over a 20-month period. Dashed lines are the uncertainty limits, and the solid line is the assigned concentration.

The analytical results have been combined to assign consensus concentrations and uncertainties to each of the samples following recommended procedures for reference materials whose concentration is determined by interlaboratory study [Ellison *et al.*, 2001]. Analyses of both S1 and D2 demonstrate that these materials are homogeneous and the concentrations have not changed in over 20 months (Figure 2). The assigned concentrations and uncertainties are 0.097 ± 0.043 nanomole per liter for S1 and 0.91 ± 0.17 nanomole per liter for D2. The uncertainty encompasses the range of results that an experienced analyst using capable methods would expect to obtain some 95% of the time.

Because of operational difficulties on board the ship, the D1 samples were not acidified until after each bottle was filled.

There was a consistent, linear decrease in concentration from 0.9 to 0.7 nanomole per liter over time and with bottle number as iron was lost from solution, presumably by adsorption of the iron that was not bound to organic molecules in solution to the tank walls. The concentration in each bottle can be predicted with reasonable confidence, based on replicate measurements by three laboratories, but the D1 samples should not be used as a reference material for field measurements. They are suitable as a reference material for method development and training. In addition, a fourth sample of coastal seawater with approximately 1.5 nanomoles per liter of iron was collected. Analysis of this sample is under way.

Each of the analytical methods used to measure iron in the SAFE samples produced

results consistent with the assigned concentrations for S1 and D2. In some cases, individual operators produced inconsistent values. The inconsistencies appear to be primarily operator oriented and not deficiencies inherent in the measurement techniques. On board ship, all measurements of iron by one method (FIA/L2; Table 1) gave inconsistent results. Further experimentation on shore with the reaction conditions used for this method (as described at <http://barbeaulab.ucsd.edu/FeLume.html>) now yield results consistent with the assigned values for S1 and D2 (K. Barbeau, personal communication, 2006).

The experiments from the SAFe cruise have shown that there is now substantial agreement between analytical methods, with systematic differences that appear to be <0.05 nanomole per liter in surface samples. This is a tenfold improvement, relative to a recent iron intercomparison [Bowie *et al.*, 2006]. Measurements on the samples have been made over a 20-month time interval with no significant changes. We recommend that all future measurements of dissolved iron in seawater should be unambiguously tied to these reference materials.

SAFe reference materials can be obtained from RequestSAFeStandard@ucsc.edu. Please provide a Federal Express billing number for shipping. At this time there is no other charge.

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Laboratory	Country	Analytical Methods ^a
Bermuda Biological Station for Research	Bermuda	FIA/DPD
Florida State University	United States	FIA/L2
Massachusetts Institute of Technology	United States	FIA/ID/MC-ICPMS
Monterey Bay Aquarium Research Institute	United States	FIA/L3
Moss Landing Marine Laboratory	United States	OE/ICPMS
Netherlands Institute for Sea Research	Netherlands	FIA/L3
Scripps Institution of Oceanography	United States	FIA/L2
University of Alaska	United States	CP/ID/HR-ICPMS
University of Brest	France	FIA/L3
University of California, Santa Cruz	United States	FIA/DPD, CSV/SA, OE/HR-GFAAS, FIA/HR-ICPMS
University of Hawaii	United States	FIA/DPD
University of Liverpool	U.K.	CSV/DHN
University of Plymouth	U.K.	FIA/L2
University of Tasmania	Australia	FIA/L2
University of Tokyo	Japan	FIA/L3
University of Victoria	Canada	CSV/DHN
University of Washington	United States	FIA/L3
Woods Hole Oceanographic Institution	United States	CSV/TAC

^aAnalytical method abbreviations are CP, coprecipitation; CSV, cathodic stripping voltammetry; DHN, 2,3-dihydroxynaphthalene; DPD, N,N-dimethyl-p-phenylenediamine; FIA, flow injection analysis; GFAAS, graphite furnace atomic absorption spectroscopy; HR-ICPMS, high-resolution-inductively coupled plasma mass spectrometry; ID, isotope dilution; L2, luminol chemiluminescence after reducing all Fe(III) to Fe(II) and no H₂O₂; L3, luminol chemiluminescence of Fe(III) with H₂O₂; MC-ICPMS, multicollector-inductively coupled plasma mass spectrometry; OE, organic extraction; SA, salicylaldehyde; and TAC, 2-(2-thiazolylazo)-p-cresol.

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